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(54) PROCESS FOR PRODUCING HETEROGENEOUS CATION EXCHANGER MEMBRANE

(57)Abstract:

PURPOSE: To provide the subject process comprising treating a heterogeneous cation exchange membrane with a resin having an ion-exchange group bridging microcracks produced at the time of after-treatment of said membrane with hot number.

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㊹不均質カチオン交換膜の製造方法

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明　細　書

1. 発明の名称　　不均質カチオン交換膜の製造方法

2. 特許請求の範囲

ポリオレフイン樹脂と微粉末状カチオン交換性物質を混合し、得られた混合物を膜状に成形し、この膜状成形物を熱水で処理した後、生じたミクロクラックの一部ないし膜表面層にカチオン交換樹脂層を形成させることを特徴とする不均質カチオン交換膜の製造方法

3. 発明の詳細な説明

本発明は改良されたカチオン交換膜の製造方法に関し、特に高イオン濃度における陽イオン輸率大なる不均質カチオン交換膜の製法に関する。イオン交換膜の一つとして線状の合成樹脂マトリックス中にイオン交換性物質を微細に分散させたものがあり、不均質イオン交換膜として実用に供されている。このような不均質イオン交換膜はイオン交換樹脂自身を膜状にした均質イオン交換膜よりも機械的強度が優れているがその機械的強度はなお充分ではなく実際に使用するに当つては種々の制約を受けている。たとえば不均質イオン交換膜の実用性を向上させるためには、イオン交換樹脂の化学構造を強固にするため、架橋度を高めて膨潤度を低くすることが必要とされているが、イオン交換基密度が犠牲となり必然的に膜の比抵抗も増大する。現在製品化されているイオン交換膜は水溶液に浸漬時とこれが空気中で自然乾燥された場合とでは膨張収縮が激しく膜の変形や膜自体にひびが入つたりすることのため実用不能となる。従つてイオン交換膜は湿潤状態に保つて貯蔵で使用することが絶対条件となつており、そのため装置として使用する場合の大きな欠点となつている。またこのようなイオン交換膜は一般に柔軟ではなく、従つてこれをイオン交換膜としてイオン交換装置に使用する場合、困難を伴うばかりでなく、イオン交換性を有するという点から興味ある他の用途に使用しようとする場合にも支障がある。

これらの点に解決を与えて新規な不均質イオン交換膜を製造することを目的として、マトリックスとしてポリオレフイン樹脂を用いてこれと微粉末状イオン交換物質を混合、成形後、熱水にて後処理を施す不均質イオン交換膜の製造方法が提案されている。この方法は、例えば特公昭47−24262号、特開昭49−63886号公報、特願昭49−53189号明細書等に示されている。しかしながら上記の方法により製造した不均質イオン交換膜は比較的低いイオン濃度の水溶液の脱塩処理用イオン交換膜としてはある程度の性能を有しており実用的ではあるが、高いイオン濃度の水溶液の脱塩処理用イオン交換膜としては性能的にはまだ充分満足しうるものではなかつた。すなわち、高いイオン濃度の水溶液において上記の方法により製造した不均質イオン交換膜の比抵抗は十分に低いがイオン輸率が低下する欠点を有していた。

上記不均質イオン交換膜は熱水後処理時におけるイオン交換樹脂の膨潤に起因してミクロクラックが発生し、これがイオン交換膜の性能の制御因子の一つとなつているが、このミクロクラックが大きいためにこの中に含まれる水またはイオンが高いイオン濃度においてイオン輸率を低下させる原因となつていると推定される。

そこで本発明者等は高いイオン濃度において膜の比抵抗を大巾に上昇させないで高いイオン輸率を有する不均質イオン交換膜を得るための方法を開発すべく種々研究した結果、不均質イオン交換膜を熱水で後処理する時生じるミクロクラックを架橋したイオン交換性の基を有する樹脂で処理することが有効である事実を発見し本発明に到達した。

すなわち、本発明は高イオン濃度における高イオン輸率の大なる不均質カチオン交換膜を提供することを目的とし、その目的は、ポリオレフイン樹脂に微粉末状カチオン交換性物質を混合し、得られた混合物を膜状に成形し、この膜状成形物を熱水にて処理した後、生じたミクロクラックの一部ないし膜表面層にカチオン交換樹脂層を形成させることを特徴とする高イオン濃度における高イオン輸率の大なる不均質カチオン交換膜の製造方法により達成することができる。

ここにおいて、マトリックス樹脂として使用されるポリオレフイン樹脂は、エチレン単独重合体、プロピレン単独重合体、エチレンまたはプロピレン主体の共重合体、およびこのようなオレフイン単独重合体または共重合体を主体とする重合体混合物を包含する。

微粉末状カチオン交換樹脂としては任意のものが用いられるが、その調製は例えば次のようにして行なわれる。

(イ) 容易にカチオン交換基の導入が可能なビニル基を有する芳香族化合物およびこれと重合能を有する不飽和結合を2個以上分子内に保有する化合物とを水性媒体中で懸濁共重合させ、得られたビーズ状共重合体をスルホン化剤で処理し、こうして得られたビーズ状カチオン交換樹脂を機械的に微粉砕する、

(ロ) 容易にカチオン交換基の導入が可能なビニル基を有する芳香族化合物およびこれと重合能を有する不飽和結合を2個以上分子内に保有する化合物とを水性媒体中で乳化重合させ、得られた微粉末状共重合体をスルホン化剤で処理して微粉末状カチオン交換樹脂とする、

(ハ) フエノール化合物／ホルムアルデヒド共縮合体を母体としたカチオン交換樹脂を機械的に微粉砕する、等の方法で行なう。

なおここでいう容易にカチオン交換基の導入が可能なビニル基を有する芳香族化合物としては、例えばスチレン、ビニルトルエン、エチルビニルベンゼン、α−メチルスチレン、ビニルナフタレンまたはその誘導体等の一種または二種以上を用いる。また重合能を有する不飽和結合を2個以上分子内に保有する化合物としては、一般にはジビニルベンゼンが用いられる。

ポリオレフイン樹脂と微粉末状カチオン交換樹脂との混合割合は製品の使用目的に応じて定められるが、一般には重量比で2：8〜8：2、

好ましくは４：６～７：３の範囲内が適当である。ポリオレフイン樹脂と微粉末状カチオン交換樹脂の混合は、両者の均一な混合を可能とする任意の方法によつて行なわれるが、一般にはロールあるいは押出機を用いて混練する。特にポリオレフイン樹脂の融点以上の温度で充分に混練するのが好ましい。この混練の段階または他の任意の段階で必要に応じて酸化防止剤、着色剤、充填剤、滑剤等の補助成分を添加することができる。次に、得られた混合物は一般的なロールあるいはプレス等で適当な条件下にフイルムあるいはシート状に成形する。成形作業の前段の可塑化工程は前記の各成分の混練工程をもつて代用することができる。

このようにして製造された膜状の成形物は、６０℃以上、好ましくは７０℃以上の熱水を用いて後処理する。本発明における熱水による処理は、比抵抗を低下させ、かつ使用中の経時変化を少なくする目的でイオン交換樹脂の膨潤を可及的大きくするために行なう。したがつて、処理用の熱水は可溶性物質を含まないことが望ましいが、ミクロクラックの発生を制御する必要があるときは、熱水に酸、アルカリあるいは塩化ナトリウム等の塩を添加することができる。

上記処理を経たイオン交換樹脂膜のミクロクラックないし膜表面層に次いでカチオン交換性樹脂層を形成する。カチオン交換樹脂層を形成する方法としては、アクリル酸のポリマー等カチオン交換性基を有するポリマーあるいはカチオン交換性基を導入しうる基を有するポリマーを溶媒に溶解し、次いで浸漬等適宜の手段によりイオン交換樹脂膜に塗布した後、放射線を照射して架橋させる方法、またはカチオン交換性モノマーと架橋用モノマーを塗布した後重合するか、あるいはカチオン交換性基を導入するに適したモノマーと架橋用モノマーを塗布重合後カチオン交換基を導入する方法等があるが、モノマーから出発する後者の方法が好適である。

すなわち、モノマーの組合せとしては大別して下記の二通りがある。

(イ) カチオン交換性基を有するモノマーと架橋用モノマーおよび場合によつては前記両モノマーと相溶する反応性あるいは非反応性溶媒。

(ロ) カチオン交換性基の導入に適したモノマーと架橋用モノマー。

カチオン交換性の基としては、カチオン交換能を有する基であればいずれも適用できるが、比抵抗の増大を防ぐにはスルホン酸基が最適である。カチオン交換性の基を有するモノマーとしては、アクリル酸、アクリル酸塩、アクリル酸エステル、メタクリル酸、メタクリル酸塩、メタクリル酸エステル、スチレンスルホン酸、スチレンスルホン酸塩、スチレンスルホン酸エステル、ビニルスルホン酸、ビニルスルホン酸塩、ビニルスルホン酸エステル等がある。

カチオン交換性基の導入に適したモノマーとしてはスチレンが一般に使用される。重合膜にカチオン交換性の基を導入する方法としては、公知の方法、例えば硫酸またはクロル硫酸によるスルホン化等が用いられる。

一方架橋用モノマーとしては、例えばジビニルベンゼン、ジメタクリレート類、メチレンビスアクリルアミド等が用いられる。カチオン交換性を有するモノマーと架橋用モノマーが相溶しない場合には、アクリル酸、メタクリル酸等の反応性のモノマーおよび／または水等の非反応性のモノマーを用いて均一系にして反応を行なう方法が良い。

上記モノマーの組合せを基体膜に含浸した後、重合を行なうが、重合方法としては紫外線、熱あるいは放射線等を用いて行なう。ただし、紫外線を用いる場合には、光増感剤として公知のベンゾイン化合物、ベンゾフエノン類、メルカプタン類等の使用が必要であり、また熱を用いる時には重合開始剤としてパーオキサイド類、アゾ化合物等の使用が必要である。重合温度としては基体膜の耐熱性、すなわちポリオレフインの耐熱性からみて１００℃以下、好ましくは８０℃以下がよい。そのために熱重合を行なう場合の開始剤は、その温度で分解するものであ

れはよく、例えはベンゾイルパーオキサイド、ラウロイルパーオキサイド、ジイソプロピルパーオキシジカーボネート、ターシャリーブチルパーオキシピバレート、アゾビスイソブチロニトリル等が用いられる。

重合後はモノマーを除去するためにメタノールで洗浄後、さらに水洗する。場合によっては、その後熱水にて膨潤後処理する。

以上のようにして得た不均質カチオン交換膜は高イオン濃度水溶液中において膜の比抵抗を損なうことなく、大巾にイオン輸率が増大する。

以下実施例により本発明をさらに詳細に説明する。なお本発明はこれら実施例に限定されるものではなく任意の変更が可能である。実施例中、部と%はすべて重量による。

〔比較例－1〕

スチレン92部に対してジビニルベンゼン（純度55％）8部を加え、過酸化ベンゾイル等を触媒として懸濁重合法により粒状共重合体を得て、これを発煙硫酸でスルホン化して強酸性カチオン交換樹脂を得た。この強酸性カチオン交換樹脂を振動ボールミルで粒度325メッシュ以下に粉砕した。この樹脂の総イオン交換容量は4.5 meq/g（乾燥樹脂）であった。粉砕した強酸性カチオン交換樹脂粉末60部に対してポリプロピレン（MI＝10）粉末40部を加えて充分に均一混合を行なった後、シート成形し膜状成形物(A)を得た。この膜状成形物(A)を温度95℃の熱水中に30分間浸漬し、不均質カチオン交換膜(B)を得た。このカチオン交換膜の膜厚は0.38㎜、イオン輸率は0.76、比抵抗は150Ω·㎝であった。

〔実施例－1〕

スチレンスルホン酸カリ51％、アクリル酸24％、メチレンビスアクリルアミド25％、ベンゾインメチルエーテル2％／モノマー、/手 および水70％／モノマーよりなる液を調製し50℃にて均一系とした後、不均質カチオン交換膜(B)を浸漬し、脱気後日本電池㈱製高圧水銀ランプTYPE I－20（出力2KW／ランプ長25㎝）を用いて照射距離10㎝の条件下で10秒照射し、改良膜を得た。この膜の厚みは0.43㎜でイオン輸率は0.94、比抵抗は250Ω·㎝であった。この膜を95℃の熱水中に30分間浸漬後の物性は膜厚み0.43㎜でイオン輸率は0.92、比抵抗は180Ω·㎝であった。

〔比較例－2〕

膜状成形物(A)を熱水処理する前に〔実施例－1〕と同じ条件でイオン交換樹脂層を形成せしめ、しかる後95℃の熱水に30分間浸漬した。

このカチオン交換膜の膜厚、イオン輸率、比抵抗はそれぞれ0.40㎜、0.78、160Ω·㎝であった。

〔実施例－2〕

スチレンスルホン酸カリの代りにビニルスルホン酸ソーダを使用した以外は〔実施例－1〕と同様の方法によってカチオン交換膜を得た。この膜を95℃の熱水中に30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.39㎜、0.86、170Ω·㎝であった。

〔実施例－3〕

メチレンビスアクリルアミドの代りにエチレングリコールジメタクリレートを使用した以外は〔実施例－1〕と同様の方法によってカチオン交換膜を得た。この膜を95℃の熱水中に30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.40㎜、0.88、230Ω·㎝であった。

〔実施例－4〕

メチレンビスアクリルアミド単独の代りにメチレンビスアクリルアミド9％とエチレングリコールジメタクリレート16％を使用した以外は〔実施例－1〕と同様の方法によってカチオン交換膜を得た。この膜を95℃の熱水中に60分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.42㎜、0.90、220Ω·㎝であった。

〔実施例－5〕

スチレン92％、ジビニルベンゼン8％、ベンゾインメチルエーテル2％／モノマーよりな

る液中に不均質カチオン交換膜(注)を浸漬し脱気後〔実施例－1〕と同様の照射装置を用いて20秒照射した。この膜を98％硫酸83％、テトラクロルエタン17％よりなる液中で40℃で6時間スルホン化した。この膜を95℃の熱水中に30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.44㎜、0.88、250Ω・㎝であつた。

〔実施例－6〕

スチレンスルホン酸カリ51％、アクリル酸24％、メチレンビスアクリルアミド25％、過硫酸アンモニウム1％／モノマー、および水70％／モノマーよりなる液中に不均質カチオン交換膜(注)を浸漬し、脱気後80℃で4時間重合し、改質膜を得た。この膜を95℃の熱水中に30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.45㎜、0.85、160Ω・㎝であつた。

〔実施例－7〕

スチレンスルホン酸カリ51％、アクリル酸24％、メチレンビスアクリルアミド25％、および水70％／モノマーよりなる液を調製し50℃にて均一系とした後、不均質カチオン交換膜(注)を浸漬し、脱気後1メガラッド電子線照射を行ない改質膜を得た。この膜を95℃の熱水中に30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.42㎜、0.90、200Ω・㎝であつた。

〔実施例－8〕

アクリル酸75％、メチレンビスアクリルアミド25％、およびベンゾインメチルエーテル2％／モノマーよりなる液を調製した後、不均質カチオン交換膜(注)を浸漬し、脱気後〔実施例－1〕と同様の装置にて20秒照射し改良膜を得た。この膜を95℃の熱水にて30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.42㎜、0.92、350Ω・㎝であつた。

〔実施例－9〕

ポリアクリル酸水溶液（ポリアクリル酸：水＝1：1）中に不均質カチオン交換膜(注)を浸漬し、脱気後1メガラッド電子線照射を行ない改質膜を得た。この膜を95℃の熱水中に30分間浸漬後の膜厚み、イオン輸率、比抵抗はそれぞれ0.41㎜、0.87、320Ω・㎝であつた。

注1）イオン輸率は膜で0.5規定の塩化ナトリウム水溶液と0.005規定の塩化ナトリウム水溶液とを隔離し、膜を介して両水溶液間に発生する膜電位より算出された。

注2）比抵抗は0.5規定の塩化ナトリウム水溶液中において交流電流を通じた時の膜の示す電気抵抗値（Ω・㎝）によつて算出された。

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TITLE (54): Method for Manufacturing Heterogeneous Cation Exchange Membrane

ABSTRACT (57):

SPECIFICATION

1. Title of the Invention

Method for Manufacturing Heterogeneous Cation Exchange Membrane.

2. Claims

A method for manufacturing a heterogeneous cation exchange membrane, characterized in that a polyolefin resin is mixed with a finely powdered cation exchangeable substance, the mixture thus obtained is molded into a membrane, and this molded membrane is treated with hot water, after which a cation exchange resin layer is formed on the membrane surface layer or part of the microcracks thus formed.

3. Detailed Description of the Invention

The present invention relates to an improved method for manufacturing a cation exchange membrane, and more particularly relates to a method for manufacturing a heterogeneous cation exchange membrane with a high cation transport number at a high ion concentration. One type of ion exchange membrane comprises an ion exchangeable substance finely dispersed in a synthetic resin matrix in the form of a membrane, and this has been put to practical use as a heterogeneous ion exchange membrane. A heterogeneous ion exchange membrane such as this has better mechanical strength than a heterogeneous ion exchange membrane produced by forming the ion exchange resin itself into a membrane, but the mechanical strength is still not adequate, and various limitations are encountered in actual use. For instance, in order to enhance the practicality of a heterogeneous ion exchange membrane, it is said that the degree of swelling has to be lowered by raising the degree of cross linking so as to strengthen the chemical structure of the ion exchange resin, but this sacrifices ion exchange group density, and the specific resistance of the membrane increases as a matter of course. The ion exchange membranes that are on the market today undergo serious swelling when dipped in an aqueous solution and serious shrinkage when dried naturally in air, so much so that the membrane becomes deformed or cracked and cannot be put to practical use. Therefore, it is an absolute requirement that the ion exchange membrane be stored in a moist state and used at normal temperature, and this poses a major obstacle to use in an apparatus. In addition, since such an ion exchange membrane generally lacks flexibility, not only are there difficulties when using this ion exchange membrane in an ion exchange apparatus, but obstacles are also met in considering use in other applications for which [this ion exchange membrane] would be interesting because of its ion exchangeability.

In an effort to solve these problems and manufacture a novel heterogeneous ion exchange membrane, a method has been proposed for manufacturing a heterogeneous ion exchange membrane by using a polyolefin resin as a matrix, mixing this with a finely powdered ion exchangeable substance, molding this mixture, then subjecting this product to post-treatment with hot water. This method is disclosed, for example, in Japanese Patent Publication 47-24262, Japanese Laid-Open Patent Application 49-43888, and Japanese

Patent Application 49-53189. Nevertheless, while a heterogeneous ion exchange membrane manufactured by the above method was practical in that it did offer a certain amount of performance as an ion exchange membrane for the desalting of aqueous solutions with relatively low ion concentrations, its performance was still lacking when it was used as an ion exchange membrane for the desalting of aqueous solutions with high ion concentrations. Specifically, in an aqueous solution having a high ion concentration, the heterogeneous ion exchange membrane prepared by the above method shows an adequately low specific resistance, but has at the same time a disadvantage that the ion transport number is considerably lowered.

In the above heterogeneous ion exchange membranes, microcracks are formed due to swelling of the ion exchange resin during the post-treatment with hot water, and this is a control factor of the performance of the ion exchange membrane. It is surmised that because these microcracks are fairly large, water or ions contained therein are the cause of the lowered ion transport number at high ion concentrations.

In view of this, the inventors conducted research aimed at developing a method for obtaining a heterogeneous ion exchange membrane that has a high ion transport number without greatly raising the specific resistance of the membrane at a high ion concentration, and as a result they arrived at the present invention upon discovering the fact that it is effective to treat the microcracks that occur during hot water post-treatment of a heterogeneous ion exchange membrane with a resin having crosslinked ion exchangeable groups.

Specifically, it is an object of the present invention to provide a heterogeneous ion exchange membrane with a high cation transport number at a high ion concentration, and this object can be achieved by a method for manufacturing a heterogeneous cation exchange membrane with a high cation transport number at a high ion concentration, characterized in that a polyolefin resin is mixed with a finely powdered cation exchangeable substance, the mixture thus obtained is molded into a membrane, and this molded membrane is treated with hot water, after which a cation exchange resin layer is formed on the membrane surface layer or part of the microcracks thus formed.

Polyolefin resins that can be used as the matrix resin here include ethylene homopolymers, propylene homopolymers, copolymers primarily consisting of ethylene or propylene, and copolymer mixtures primarily consisting of one of these olefin homopolymers or copolymers.

Any finely powdered cation exchange resin can be used, but the preparation thereof is carried out as follows, for example:

(A) An aromatic compound that has vinyl groups allowing for the easy introduction of cation exchange groups is subjected to suspension copolymerization in an aqueous medium with a compound that has two or more unsaturated bonds per molecule and that can be polymerized with this aromatic compound, the copolymer beads thus obtained are treated with a sulfonation agent, and the cation exchange resin beads obtained in this manner are mechanically pulverized.

(B) An aromatic compound that has vinyl groups allowing for the easy introduction of cation exchange groups is subjected to emulsion polymerization in an aqueous medium with a compound that has two or more unsaturated bonds per

molecule and that can be polymerized with this aromatic compound, and the finely powdered copolymer thus obtained is treated with a sulfonation agent to obtain a finely powdered cation exchange resin.

(C) A cation exchange resin whose matrix is a copolymer of a phenol compound and formaldehyde is mechanically pulverized.

Examples of the "aromatic compound that has vinyl groups allowing for the easy introduction of cation exchange groups" referred to here include styrene, vinyltoluene, ethylvinylbenzene, α-methylstyrene, vinylnaphthalene, and derivatives of these. These compounds can be used singly or in combination. Divinylbenzene is generally used as the "compound that has two or more unsaturated bonds per molecule and that can be polymerized."

The mixing ratio of the polyolefin resin and the finely powdered cation exchange resin is determined as dictated by the intended use of the finished product, but is generally 2:8 to 8:2 by weight, with a preferable range being 4:6 to 7:3 by weight. The mixing of the polyolefin resin and the finely powdered cation exchange resin can be accomplished by any method that allows the two components to be mixed uniformly, but kneading is generally performed using a roll or an extruder. Particularly desirable is thorough kneading at a temperature over the melting point of the polyolefin resin. Other auxiliary components such as antioxidants, colorants, fillers, and lubricants can be added as needed during this kneading or at any other stage. The obtained mixture is then molded into a film or sheet under suitable conditions in an ordinary roll or press. The plasticizing step that comes before the molding work can be replaced by the step in which the above-mentioned components are kneaded.

The film-shaped article manufactured in this way is subjected to a post-treatment with hot water at 60°C or higher, and preferably 70°C or higher. The hot water treatment is performed in the present invention in order to increase the swelling of the ion exchange resin as much as possible for the purpose of lowering the specific resistance and minimizing changes over time as the product is used. It is therefore preferable for the hot water used in the treatment not to contain any soluble substances, but if it is necessary to control the formation of microcracks, an acid, an alkali, or a salt such as sodium chloride can be added to the hot water.

A cation exchange resin layer is then formed on the membrane surface layer or the microcracks in the ion exchange resin membrane that has undergone this treatment. This cation exchange resin layer can be formed, for example, by a method in which a polymer that has cation exchangeable groups, such as a polymer of acrylic acid, or a polymer that has groups allowing the introduction of cation exchangeable groups is dissolved in a solvent, and [this solution] is then applied to the ion exchange resin membrane by a suitable means such as dipping, after which [this coating] is crosslinked by irradiation, or by a method in which a cation exchangeable monomer and a crosslinking monomer are applied and then polymerized, or a monomer suited to the introduction of cation exchangeable groups and a crosslinking monomer are applied and polymerized, and cation exchange groups are then introduced. The latter method, which starts from monomers, is preferred, however.

Specifically, the combination of monomers can be broadly classified into two groups as follows.

(A) Monomers having cation exchangeable groups and crosslinking monomers, and in some cases reactive or non-reactive solvents that are miscible with both of the above monomers.

(B) Monomers suited to the introduction of cation exchangeable groups and crosslinking monomers.

Any groups able to undergo cation exchange can be employed as the cation exchangeable groups, but sulfonic acid groups are preferred for the purpose of preventing an increase in specific resistance. Examples of monomers having cation exchangeable groups include acrylic acid, acrylic salts, acrylic esters, methacrylic acid, methacrylic salts, methacrylic esters, styrenesulfonic acid, styrenesulfonic salts, styrenesulfonic esters, vinylsulfonic acid, vinylsulfonic salts, and vinylsulfonic esters.

Styrene is generally used as the monomer suited to the introduction of cation exchangeable groups. A known method, such as sulfonation by sulfuric acid or chlorosulfuric acid, can be used as the method for introducing the cation exchangeable groups after polymerization.

Meanwhile, divinylbenzene, a dimethacrylate, methylenebisacrylamide, or the like can be used as the crosslinking monomer. If the monomer having cation exchangeable groups and the crosslinking monomer are not miscible, then it is better to conduct the reaction as a uniform system by using acrylic acid, methacrylic acid, or another such reactive monomer and/or water or another such non-reactive monomer.

A substrate membrane is impregnated with the above-mentioned combination of monomers, after which polymerization is conducted, and the polymerization method can involve the use of ultraviolet rays, heat, radiation, or the like. When UV rays are used, however, a known benzoin compound, a benzophenone, a mercaptan, or the like must be used as a photosensitizer, and when heat is used, a peroxide, an azo compound, or the like must be used as a polymerization initiator. In view of the heat resistance of the substrate membrane, that is the heat resistance of the polyolefin, the polymerization temperature should be 100°C or lower, and preferably 80°C or lower. Accordingly, the initiator used when thermal polymerization is conducted should be one that will decompose at this temperature, examples of which include benzoyl peroxide, lauroyl peroxide, diisopropyl peroxydicarbonate, tert-butyl peroxypivalate, and azobisisobutyronitrile.

After polymerization, [the product] is washed with methanol and then with water in order to remove the monomers. In some cases, a post-treatment with hot water is performed once more after this.

A heterogeneous cation exchange membrane obtained in the above manner will have a greatly increased ion transport number without any loss of the specific resistance of the membrane in an aqueous solution with a high ion concentration.

The present invention will now be described in further detail through working examples. The present invention is not limited to these working examples, and modifications can be made within the scope of the present invention. All parts and percentages in the working examples are by weight.

Comparative Example 1

8 parts of divinylbenzene (55% purity) was added to 92 parts of styrene, and copolymer particles were obtained by suspension polymerization using benzoyl peroxide or the like as

a catalyst. This product was sulfonated with fuming sulfuric acid to obtain a strongly acidic cation exchange resin. This strongly acidic cation exchange resin was ground to a grain size of 325 mesh or less in a vibrating ball mill. This resin had a total exchange capacity of 4.5 meq/g on dry base. 40 parts of polypropylene (MI = 10) powder was added to 60 parts of this ground strongly acidic cation exchange resin and subjected to thorough agitation and mixing, after which this mixture was sheet-molded to obtain a molded membrane (A). This molded membrane (A) was soaked for 30 minutes in 95°C hot water, which yielded a heterogeneous cation exchange membrane (B). The thickness of this cation exchange membrane was 0.38 mm, the ion transport number was 0.76, and the specific resistance was 150 Ω · cm.

Working Example 1

A solution composed of 51% potassium styrenesulfonate, 24% acrylic acid, 25% methylenebisacrylamide, 2%/monomer benzoin methyl ether, and 70%/monomer water was prepared and made into a homogeneous system at 50°C, after which the heterogeneous cation exchange membrane (B) was immersed in this solution, and after deaeration, this product was irradiated for 10 seconds at an irradiation distance of 10 cm using a Type I-20 high pressure mercury vapor lamp made by JEOL (output: kW, lamp length: 25 cm), which yielded a modified membrane. The thickness of this membrane was 0.45 mm., its ion transport number was 0.94, and its specific resistance was 230 Ω · cm. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.43 mm, its ion transport number was 0.93, and its specific resistance was 180 Ω · cm.

Comparative Example 2

An ion exchange resin layer was formed under the same conditions as in Working Example 1 prior to the hot water treatment of the molded membrane (A), after which this product was soaked for 30 minutes in 95°C hot water.

The thickness of this cation exchange membrane was 0.40 mm, its ion transport number was 0.78, and its specific resistance was 160 Ω · cm.

Working Example 2

Other than using sodium vinylsulfonate in place of the potassium styrenesulfonate, a cation exchange membrane was obtained by the same method as in Working Example 1. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.39 mm, its ion transport number was 0.86, and its specific resistance was 170 Ω · cm.

Working Example 3

Other than using ethylene glycol dimethacrylate in place of the methylenebisacrylamide, a cation exchange membrane was obtained by the same method as in Working Example 1. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.40 mm, its ion transport number was 0.88, and its specific resistance was 230 Ω · cm.

Working Example 4

Other than using 9% methylenebisacrylamide and 16% ethylene glycol dimethacrylate in place of methylenebisacrylamide alone, a cation exchange membrane was obtained by the same method as in Working Example 1. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.42 mm, its ion transport number was 0.90, and its specific resistance was 220 Ω · cm.

Working Example 5

The heterogeneous cation exchange membrane (B) was immersed in a solution composed of 92% styrene, 8% divinylbenzene, and 2%/monomer benzoin methyl ether, after which this product was irradiated for 20 seconds using the same irradiation apparatus as in Working Example 1. This membrane was sulfonated for 6 hours at 40°C in a solution composed of 83% sulfuric acid (98%) and 17% tetrachloroethane. This membrane was then soaked for 30 minutes in 95°C hot water, after which its thickness was 0.44 mm, its ion transport number was 0.88, and its specific resistance was 230 Ω · cm.

Working Example 6

The heterogeneous cation exchange membrane (B) was immersed in a solution composed of 51% potassium styrenesulfonate, 24% acrylic acid, 25% methylenebisacrylamide, 1%/monomer ammonium persulfate, and 70%/monomer water, and after deaeration, this product was polymerized for 4 hours at 80°C to obtain a modified membrane. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.43 mm, its ion transport number was 0.85, and its specific resistance was 160 Ω · cm.

Working Example 7

A solution composed of 51% potassium styrenesulfonate, 24% acrylic acid, 25% methylenebisacrylamide, and 70%/monomer water was prepared and made into a homogeneous system at 50°C, after which the heterogeneous cation exchange membrane (B) was immersed in this solution, and after deaeration, this product was irradiated with a one-megarad electron beam to obtain a modified membrane. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.42 mm, its ion transport number was 0.90, and its specific resistance was 200 Ω · cm.

Working Example 8

A solution composed of 75% acrylic acid, 25% methylenebisacrylamide, and 2%/monomer benzoin methyl ether was prepared, after which the heterogeneous cation exchange membrane (B) was immersed in this solution, and after deaeration, this product was irradiated for 20 seconds using the same irradiation apparatus as in Working Example 1 to obtain a modified membrane. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.42 mm, its ion transport number was 0.92, and its specific resistance was 350 Ω · cm.

Working Example 9

The heterogeneous cation exchange membrane (B) was immersed in a polyacrylic acid aqueous solution (polyacrylic acid:water - 1:1), and after deaeration, this product was

irradiated with a one-megarad electron beam to obtain a modified membrane. This membrane was soaked for 30 minutes in 95°C hot water, after which its thickness was 0.41 mm, its ion transport number was 0.87, and its specific resistance was 320 Ω · cm.

Note 1: The ion transport number was calculated from the membrane potential generated between a 0.5 N sodium chloride aqueous solution and a 0.005 N sodium chloride aqueous solution when the two aqueous solutions were separated by the membrane.

Note 2: Specific resistance was calculated from the electrical resistance (Ω · cm) exhibited by the membrane when an alternating current was passed through a 0.5 N sodium chloride aqueous solution.

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